

# PATENT SPECIFICATION

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## (54) PROCESS FOR PRODUCING PROPYLENE OXIDE

(71) We, SNAM PROGETTI S.p.A., an Italian Company, of Corso Venezia, 16, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing propylene oxide.

The preparation of alkylene oxides by reaction between an olefin and oxygen in the presence of a catalyst based on silver and/or silver oxide is known.

In particular, industrial processes for the production of ethylene oxide from ethylene and oxygen or air have been developed and marketed for a considerable time. Until now, however, the production of higher alkylene oxides by a similar synthesis, particularly propylene oxide, which is mainly produced indirectly, has not been an attractive commercial proposition.

In French Patent Specification No. 785,149 it was proposed to produce propylene oxide from propylene and oxygen in the presence of a silver-based catalyst by feeding extremely large quantities of inert compounds, in particular carbon dioxide or water vapour,

together with the reagents, to the catalyst-containing zone. However, the results obtained by such a process are not satisfactory from an industrial point of view.

It is therefore particularly surprising to find that it is possible to obtain propylene oxide in a high selectivity when water vapour in the range from 2 to 25% by volume of the sum of propylene, oxygen and water vapour, is added to the reaction mixture.

Accordingly, the present invention provides a process for producing propylene oxide, which comprises reacting propylene with oxygen or a gaseous mixture including oxygen, in the presence of a silver-based catalyst and in the presence of water vapour in a quantity in the range from 2 to 25% by volume of the sum of the volumes of the propylene, oxygen and water vapour present.

It has been found that if the quantity of water vapour is higher than 30% by volume the selectivity with respect to propylene oxide is not merely not further increased but is significantly reduced.

The term "selectivity" when used herein with respect to propylene oxide is defined as follows:—

$$\left( \frac{\text{number of moles of propylene oxide produced}}{\text{number of moles of propylene which have reacted}} \right) \times 100.$$

Preferably the process of the present invention is effected by introducing propylene, air (or oxygen) and water vapour in the appropriate relative quantities over a silver-based catalyst in a reactor maintained at a temperature in the range from 110 to 400°C.

Preferably the ratio by volume of propylene to oxygen (or oxygen in air) in the reactor is in the range from 4:96 to 95:5. The quantity of water vapour present is in the range from 2 to 25% with respect to the total of the propylene, oxygen, and water vapour in the feed gas, preferably from 2 to 15%.

In the feed gas, gaseous compounds which do not influence negatively the reaction can be present. Silver-based catalysts which can be used with advantage in the present invention are those based on metallic silver or silver compounds.

This silver-based catalyst can also contain lesser quantities of other elements as activators such as magnesium, calcium, barium, strontium, selenium, tellurium, lead, tin, arsenic, or compounds containing such elements.

The catalyst can be used unsupported or it can be suitably supported, for example on

a silicate of alumina (china clay), carborundum or kieselguhr support.

It is possible to introduce into the reaction zone a suitable inhibitor which regulates the reaction rate, either before or during the reaction of propylene and oxygen. Inhibitors which can be used with advantage can be chosen from organic or inorganic chlorides.

The following Examples illustrate the present invention.

#### EXAMPLE 1.

Two tests were carried out at a constant temperature, in the absence of water and with 5%  $H_2O$  in a mixture of propylene and oxygen. When water is present, its concentration is based on the total feed of water, oxygen and propylene. The tests were carried out in the presence of a catalyst prepared in the following way.

100 G. of  $AgNO_3$ , 24 g. of calcium nitrate tetrahydrate and 11 g. of barium nitrate were dissolved in 1500 cc of deionized water, the atomic ratio Ag:Ca:Ba being 15:2.5:1.

The solution obtained, which can be opalescent due to the presence of a small quantity of silver chloride formed, was filtered through an adsorbent medium.

42 G. of anhydrous sodium carbonate were dissolved in 500 cc of distilled water and purified by the addition of 2 g. of silver nitrate. The solution obtained was filtered. A small quantity of calcium chloride was added (~10 mg.).

The coprecipitation of silver, calcium and barium carbonate was carried out by adding, under rapid agitation, the solution of sodium carbonate to the solution of the nitrates. The carbonate precipitate was obtained in a finely divided state.

The material obtained was filtered, washed with deionized water and dried for several hours in an oven at  $110^\circ C$ . with a slow air flow. About 120 g. of catalytic powder was obtained which was finely ground in a hammer mill. The catalytic material was then supported on a suitable support.

A commercial material was chosen as a support, namely silicate of alumina (china clay) with the following characteristics (alumina S.A. 5218 of Norton):

Shape: spherical; diameter 5/16"

#### Composition:

$Al_2O_3$	85.50	$TiO_2$	0.10	$Na_2O$	0.30
$SiO_2$	12.40	$MgO$	0.60	$K_2O$	0.50
$Fe_2O_3$	0.20	$CaO$	0.40		

Chemical-physical characteristics (X-ray):  $\alpha-Al_2O_3$  + Mullite

Porous structure: porosity in volume = 50.8%; pore radius: 100—700 microns.

This support possesses a particularly suitable porous structure in that it allows complete

penetration of the catalytic material throughout the interior of the spheres. Other types of alumina and other supports having the same or similar properties could be used.

Introduction of the catalytic material into and on the support was carried out by mixing the catalytic powder (obtained as above) with 800 g. of ethylene glycol and treating the resulting suspension with 550 g. of support maintained under agitation to facilitate uniform distribution.

The material obtained was then dried and activated in a controlled airflow at a temperature of approximately  $350^\circ C$  for some hours. This supported catalyst, in order to carry out the aforementioned tests, was introduced into a reactor which was 30 cm. long and 1" in diameter and which was thermostatically controlled by dowtherm circulation.

The test conditions were as follows:

Pressure = atmospheric

Catalyst volume = 100  $cm^3$

gas flow = 5Nl/hour

Molar ratio of  $C_3H_6 : O_2 = 85 : 15$

The test results are reported in the following Table 1.

#### EXAMPLE 2.

The same reactor as described in Example 1 was used; the active part of the catalyst consisted of Ag alone and the 10 mg. of  $CaCl_2$  were not added. The test results and the reaction conditions are reported in Table 1.

#### EXAMPLE 3.

The same reactor as described in Example 1 was used; the active part of the catalyst was prepared starting from 100 g. of  $AgNO_3$  and 32.4 g. of  $Co(NO_3)_2 \cdot 4H_2O$ .

$CaCl_2$  was not used. The test results and reaction conditions are reported in Table 1.

#### EXAMPLE 4.

The same reactor as described in Example 1 was used; the active part of the catalyst was prepared starting from 100 g. of  $AgNO_3$  and 35.9 g. of  $Ba(NO_3)_2$ .  $CaCl_2$  was not used. Test results and operating conditions are reported in Table 1.

#### EXAMPLE 5.

Another catalyst was prepared by a method which involved impregnation of a support with solutions of the active components. It consisted in the preparation of solutions of organic silver salts and promoters, and then the impregnation of the support with such solutions.

A general procedure is to maintain the temperature around  $90$  to  $95^\circ C$ . during the operation for a variable duration depending on the type of support; however, not more than an hour later, the solution is removed and the

impregnated material maintained at 90 to 95°C for a further 15 minutes.

- 5 The material was then placed in an oven at 70 to 80°C. in a slow air flow for about 12 hours; after which it was subjected to calcination at 320°C for about 5 hours in a controlled air flow. The test was carried out in the same reactor as described in Example 1. The catalyst was prepared starting from 10 100 g. of Ag lactate and 0.8 g. of Ba lactate. The support consisted of alumina spheres of a diameter equal to 3/16". The test results and operating conditions are reported in Table 1.

#### EXAMPLE 6.

- 15 40 G. of the powder constituting the active part of the catalyst described in Example 1 were introduced into a glass reactor of one inch diameter, which was heated by means of a dowtherm circulation. Some tests on the synthesis of propylene oxide were carried out on this catalyst with a stream of propylene and oxygen, and with constant temperature and different H<sub>2</sub>O content. The conditions under which the tests were carried out are as follows: 25

Pressure=atmospheric  
Temperature=184°C  
Reagent mixture flow=5Nl/hour  
Molar ratio of C<sub>3</sub>H<sub>6</sub>:O<sub>2</sub>=85:15

The results are reported in the following Table 2. 30

#### EXAMPLE 7.

Tests relating to the propylene oxide synthesis from propylene and oxygen were carried out using a catalyst made up of silver powder, with different water contents in the gas feed. 35

The reactor used was the same as in previous Examples and the reaction conditions were as follows: 40

Pressure=atmospheric  
Reagent mixture flow=5Nl/hour  
Temperature=181°C  
Molar ratio of C<sub>3</sub>H<sub>6</sub>:O<sub>2</sub>=85:15

The test results are summarised in the following Table 3. 45

TABLE 1

Example No.	Atomic Ratio Ag:Ca:Ba	Feed C <sub>3</sub> H <sub>6</sub> :O <sub>2</sub> (% mols)	T °C.	Selectivity (% mol)	
				without H <sub>2</sub> O	with 5% H <sub>2</sub> O
1	15:2.5:1	85:15	195	24.4	50.0
2	15: 0 :0	85:15	215	6.0	21.0
3	15:3.5:0	85:15	193	8.9	24.5
4	15: 0:3.5	85:15	195	12.0	23.5
5	1400:0:7.9	85:15	210	3.5	7.0

TABLE 2

% H <sub>2</sub> O	Selectivity (% mol)
0	35
4	52
5	49
8	49
12	51
14	45
33	37
47	18

TABLE 3

% H <sub>2</sub> O	Selectivity (% mol)
0	30.5
6.5	41.6
17.5	34.4
48.5	10

## WHAT WE CLAIM IS:—

1. A process for producing propylene oxide, which comprises reacting propylene with oxygen or a gaseous mixture including oxygen, in the presence of a silver-based catalyst and in the presence of water vapour in a quantity in the range from 2 to 25% by volume of the sum of the volumes of the propylene, oxygen and water vapour present.

2. A process according to Claim 1, wherein the quantity of water vapour introduced is in the range from 2 to 15% by volume of the sum of the volumes of the propylene, oxygen and water vapour present.

3. A process according to Claim 1 or 2, wherein the reaction is carried out at a temperature in the range from 110 to 400°C.

4. A process according to Claim 1, 2 or 3, wherein the molar ratio of propylene to oxygen is in the range from 4:96 to 95:5.

5. A process according to any preceding claim, wherein the gaseous mixture including oxygen is air.

6. A process according to any preceding claim, wherein a mixture of propylene, oxygen or gaseous mixture including oxygen, and water vapour is passed over the silver-based catalyst in a heated reaction zone.

7. A process according to any preceding claim, wherein the silver-based catalyst includes one or more of magnesium, calcium, barium, strontium, selenium, tellurium, lead, tin and arsenic.

8. A process according to Claim 1, substantially as described in any one of the foregoing Examples.

9. Propylene oxide whenever produced by a process according to any preceding claim.

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